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Oxidation of Iron(II) in Acidic Chloride Solutions

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An experimental study was made of oxidation with air at below 80°C of iron(II) chloride solutions with $2 \leq pH \leq 5$. During the course of oxidation the pH was kept at a constant value by varying the ammonia content in air. It has been found that the formation of γ-FeO(OH) with or without α-FeO(OH) takes place by selecting the pH and oxidation temperature, and that the presence of extremely fine γ-FeO(OH) particles in the iron(II) chloride solution facilitates the formation of needle-like γ-FeO(OH) particles by oxidation.

KEY WORDS: Iron(II) chloride solution/ Green rust I/ γ-FeO(OH)/ Needle-like particles/ Air oxidation/

INTRODUCTION

When a small amount of an alkaline solution is added to an acidic solution of iron(II) chloride, a neutral suspension of whitish precipitate with a blue tint is obtained. After the transformation of the precipitate into green rust I by a slow oxidation with air, γ-FeO(OH) begins to be formed in the dark blue suspension with pH 6 at temperatures lower than those for the formation of Fe_3O_4. The pH decreases rapidly to below 5 with the disappearence of green rust I by oxidation.[1)]

γ-FeO(OH) can be obtained by the air oxidation of an acidic solution of iron (II) salt by selecting the kinds of acid anions present and the oxidation temperature. Depending on the temperature the formation of either α-FeO(OH) or iron(III) hydroxide takes place in an iron(II) chloride solution by oxidation. As the precipitation proceeds by oxidation, the pH decreases and β-FeO(OH) begins to be formed at $pH < 2$.[2)]

It is possible to keep the pH at a constant value while the precipitation occurs in the acidic solution by oxidation, provided that the rate of the neutralization of HCl formed is adjusted. The air oxidation at temperatures 15–80°C of iron(II) chloride solutions was carried out. During the oxidation, the pH was kept constant in the range $2 \leq pH \leq 5$ by controlling the NH_3 content in air. It was found that the formation of precipitates of α-, β-, γ-FeO(OH) and α-Fe_2O_3, or an amorphous precipitate took place, depending on the pH and the oxidizing temperature.

In this paper the experimental results will be reported on the oxidation products and on the conditions favorable for the formation of γ-FeO(OH).

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EXPERIMENTAL

Figure 1 shows the reaction vessel specially constructed for the air oxidation experiments; it was a partially tapered cylinder made of hard polyvinyl chloride, 70 cm in height with internal diameters of 2.0 and 12.7 cm at the neck and the cyllindrical portion, respectively.

A perforated plate made of stainless steel was 0.1 cm in thickness and had five holes with 0.1 cm in dia. arranged at a uniform distance. It was sandwiched between flanges at the neck portion and at the upper end of gas holder, and they were bolted together. The vessel was closed with ruber stoppers, into which the same parts as previously described had been inserted.[3)]

The air for stirring and oxidation was passed through washing vessels containing a KOH solution to remove carbon oxide and dust. The acidic solution was prepared by dissolving 1.2 mol $FeCl_2 \cdot 4H_2O$ into 0.6 M (1 M=mol dm^{-3}) HCl (1 L*)

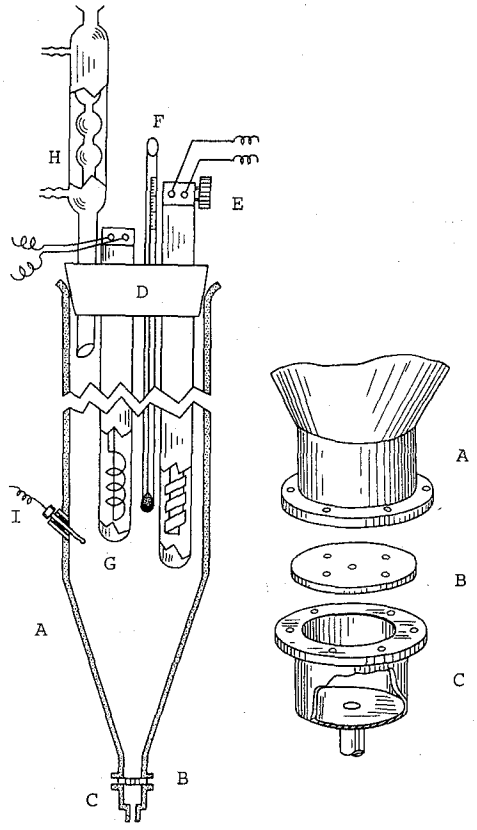

Fig. 1. An illustration of the reaction vessel used.
A: Partially tapered cylindrical vessel,
B: Perforated plate, C: Gas holder,
D: Rubber stopper, E: Thermoregulator,
F: Thermometer, G: Heater,
H: Condenser,
I: Glass electrodes for a self-recording pH meter.

* L=dm^3

both of analytical grade, and diluted with water to 5 L. The acidic solutions, each containing 0.24 M Fe(II) and 0.12 M HCl, were subjected to oxidation as follows.

Air was bubbled into the vessel from its bottom through the perforated plate at a rate of 50 L/h. While bubbling air, each 5 L acidic solution was poured into the vessel from its top. The solution was quickly heated to a desired temperature. After it had been reached, NH_3-containing air was bubbled at a rate of 500 L/h. During oxidation the temperature and pH of the solution were kept constant and several 100 mL portions were taken out at intervals from the suspension. The pH value was kept constant by controlling the ammonia content in air. Each oxidation product was filtered, washed with water, and dried at 80°C in air.

Each sample was examined by X-ray diffraction using Mn filtered FeKα radiation. Some were further examined by electronmicroscopic observation, and BET surface area determination using nitrogen.

RESULTS AND DISCUSSION

At the end of precipitation by oxidation, the pH value increased rapidly to 7 or greater. The rate of precipitation by oxidation became extremely smaller with decrease in the pH and/or temperature. When the time of oxidation required, t min, for the completion of the precipitation was longer than 50 h, the oxidation was stopped at 50 h, though the iron(II) still remained.

Table I. Typical samples obtained at various pH values and oxidation temperatures T.

pH	T/°C	t/min	Product	S/m^2 g^{-1}
4.5	50	360	α-FeO(OH)=γ-FeO(OH)	
3.5	50	804	γ-FeO(OH)	54.6
3.0	50	—	α-FeO(OH)=γ-FeO(OH)	
2.5	50	—	α-FeO(OH)	126.9
3.5	80	318	α-FeO(OH)$\gg\alpha$-Fe_2O_3	
4.0	40	—	γ-FeO(OH)>α-FeO(OH)	
5.0	15	—	γ-FeO(OH)>α-FeO(OH)	63.7

The properties of typical oxidation products prepared under various conditions are given in Table I, together with the t. The oxidation at 80°C caused the formation of α-Fe_2O_3 with α-FeO(OH) for pH$\leq$3.5 or of Fe_3O_4 for pH$\geq$4.5 and the oxidation at pH 2.0 resulted in the formation of β-FeO(OH) with α-FeO(OH), or of an amorphous precipitate at below 70°C. As evident from Table I, γ-FeO(OH) is formed with or without α-FeO(OH) in the range 3.0$\leq$pH$\leq$5.0 depending on the temperature.

In the case of forming the mixture of α-FeO(OH) and γ-FeO(OH), the γ-FeO(OH) content in the intermediate oxidation product during the course of oxidation is slightly affected by the concentration of the remaining iron(II) as shown in Fig. 2. The ultimate oxidation product was found to consist of bur-like par-

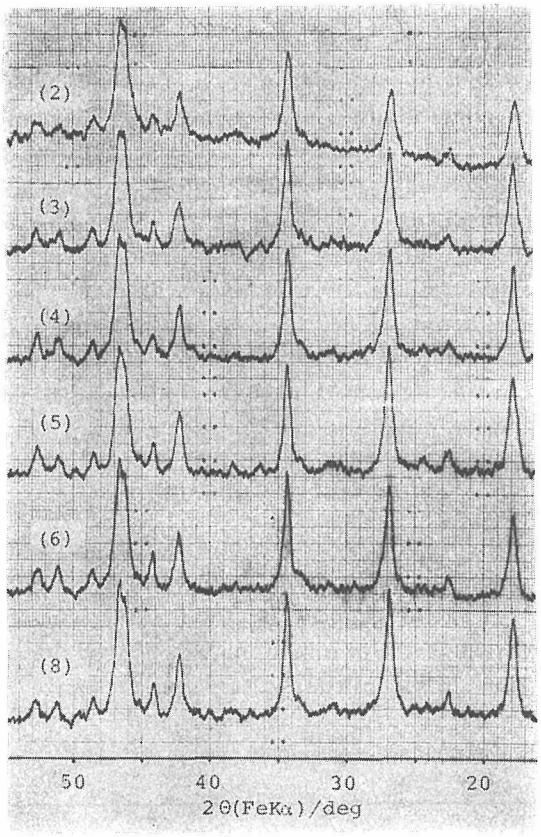

Fig. 2. X-ray diffraction patterns of precipitates during the course of oxidation at 60°C of Fe(II) at pH 4.0. Number in parentheses indicates the time of oxidation in h.

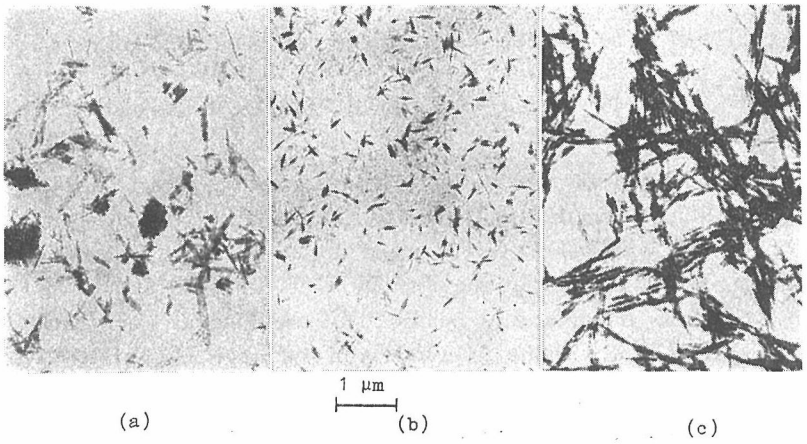

Fig. 3. Electronmicrographs of oxidation products prepared at 60°C of Fe(II) at pH 4.0 in the absence (a) or presence (c) of γ-FeO(OH) seeds (b). (a) consisted of α- and γ-FeO(OH).

ticles, 1–2 μm in size, each composed of a number of fine needle-like particles (probably α-FeO(OH)), and plate-like particles (probably γ-FeO(OH)) (Fig. 3 (a)).

From our previous paper,[4] the presence of γ-FeO(OH) seeds is considered to be favorable for the formation of γ-FeO(OH) in the iron(II) chloride solution by oxidation. 40% of iron(II) in the acidic solution (1 L), containing 1.2 M $FeCl_2$ and 0.6 M HCl, was neutralized with a NaOH solution, and diluted with water to 5 L. The neutral suspension in the vessel (Fig. 1) was subjected to oxidation at 10–15°C by bubbling NH_3-eliminated air into the suspension at a constant rate of 500 L/h. The air-flow rate was decreased to 50 L/h as soon as the pH decreased below 5 due to the disappearence of green rust I, and the brownish suspension, containing Fe(II) and very fine, flaky particles of γ-FeO(OH) (Fig. 3(b)), was quickly heated to 60°C in 50 min. Oxidation at 60°C was carried out by bubbling NH_3-containing air into the suspension at a constant rate of 500 L/h. During the oxidation the pH was kept at 4 and rapidly increased above 7 in the absence of the Fe(II). The oxidation product was found by X-ray and electronmicroscopic examinations to consist only of needle-like γ-FeO(OH) particles (Fig. 3(c)).

The particle size and shape distributions of such needle-like particles could be controlled by varying the amount and size of flaky γ-FeO(OH) particles used as the seed: this mean particle-size increased with the increase in the amount of green rust I in the $2NaOH/FeCl_2$ range 0.25–0.45 or with decreasing the flow rate in the range 300–600 L/h.

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